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(54) **Nonionically and partially anionically stabilized waterdispersible graft copolymers.**

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DescriptionTechnical Field

5 This invention relates to water-dispersible polymers useful in the preparation of automotive coating formulations. More particularly, the present invention concerns water-dispersible graft polymers having utility as principal resins and as pigment grind resins in automotive coating compositions. This invention also concerns coating compositions containing such polymers, and articles of manufacture coated with such coating compositions.

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Background of the Invention

British Patent specification 1453429 and its German equivalent OS 2535503 describe photocurable compositions that are curable by actinic radiation. Such compositions comprise a vinylurethane compound,
 15 a photosensitizer and optionally a polymerisable ethylenically unsaturated liquid monomer. The vinyl urethane is obtained by reaction of isophorone diisocyanate with an ethylenically unsaturated monohydric alcohol and optionally a polyhydric alcohol having a molecular weight of less than 3,000.

European Patent Publication 167188 describes the production of ethylenically unsaturated aqueous urethane dispersions by reacting a polymerizable acrylate with a diisocyanate and then reacting the product
 20 with polyisocyanates and a further active hydrogen-containing organic compound capable of forming a soft group. This pre-polymer may then be subjected to chain extension.

Multi-layer coating systems are well known in the coatings industry. One area in which multi-layer coating systems have become increasingly utilized is the area of decorative and protective coatings for automotive vehicles. A common multi-layer coatingsystem for automotive application is the so-called "base
 25 coat/top coat" system in which a thicker layer of clear, unpigmented topcoat is applied over an underlying thinner layer of pigmented base coat. The base coat may contain reflective particulate flake materials such as aluminum flake or mica flake to impart "sparkle" to so-called metallic finishes.

These base coat/top coat coating systems may comprise either "wet-on-wet" one-bake systems in which the clear top coat layer is applied over an unbaked base coat layer with both layers being cured in a
 30 single subsequent bake curing step, or "multiple-bake" systems in which a clear coat is applied and cured over previously applied and cured base coats. Modern multi-layer coatings systems are typically of the wet-on-wet one-bake type which eliminate or minimize problems of adherence between the layers which may sometimes result with multiple-bake systems.

Early base coat/top coat coating systems for automotive applications generally comprised solvent-borne, pigmented base coat compositions and solvent-borne clear coat compositions. However, rising costs
 35 of solvents and the growing concern over the environmental impact of organic solvents has forced research efforts in recent years to turn toward means for eliminating or minimizing the organic solvent content of coating compositions.

A certain degree of success has been achieved in lowering the total volatile organic content (VOC) of
 40 multi-coat systems by reducing the organic content of both the base coat and top coat compositions. For example, recent developments in multilayer coating systems have seen the introduction of water-borne base coat compositions. One example of such water-borne systems is disclosed in US-A-4,794,147 which employs as principal resin and/or pigment grind resin a water-dispersible polyurethane resin. Coating formulations based upon these water-borne polyurethane resins can generally be applied to substrates over
 45 a broader range of ambient temperature and humidity conditions. Another type of water-borne system is exemplified by anionically stabilized acrylic resins of the type disclosed in US-A-4,403,085 and 4,518,724. Acrylic resins are generally characterized by good durability and weatherability, but sometimes suffer from the shortcoming that they must be applied within a narrow range of temperatures and humidities to avoid problems of flow and sag.

50 Anionically stabilized acrylic resins are typically formed by the polymerization of a mixture of acrylic monomers which contains a certain fraction of carboxyl group-containing monomers such as acrylic acid or methacrylic acid. The resin is dispersed in water and stabilized in aqueous medium by conversion of at least a portion of the carboxyl groups to carboxylate salt groups by neutralization with a base, typically a tertiary amine.

55 Present-day commercially viable clear top coats typically are based upon alkylated melamine resins which are thermally cross-linked in the presence of one or more acid catalysts well known in the art. Acrylic resins which are cross-linked by melamine resins are presently the resins of choice for top coats because of their exceptional gloss and durability, qualities which are highly desirable for the clear top coat in a multi

layer automotive coating system. A thorough discussion of so-called "monomeric" highly alkylated melamine resins and "polymeric" less highly alkylated melamine resins can be found in Hirsch, Albert J., "50 Years of Amine Coating Resins," the Winchell Co., Philadelphia, PA, 1986.

The highly alkylated melamine resins generally require strong acid catalysis for curing, while the less highly alkylated melamines can be cured by the use of weaker, general acid catalysts. However, in either case, organic solvents are usually required to prepare melamine-containing clear coat formulations. The highly alkylated monomeric melamine resins typically form less viscous solutions in organic solvents, permitting higher solids loading, with attendant reduction in VOC. The less-alkylated, polymeric melamine resins, on the other hand, form more viscous solutions and cannot generally be employed to form high solids clear coat formulations.

With the introduction of acrylic anionically stabilized water-borne base coat compositions, and the desire to use high solids clear coats to reduce VOC, compatibility problems have arisen. The preferred highly alkylated monomeric melamine top coat resins, requiring strong acid catalysis for curing are generally not entirely compatible with anionically stabilized base coat resins. In wet-on-wet one-bake systems where the base coat resins are of the amine-neutralized carboxyl function-containing type, amine which is freed from the base coat layer during the baking step often neutralizes a portion of the strong acid catalyst employed to cure the highly alkylated melamine resins in the top coat. This can sometimes result in an incompletely cured top coat layer with attendant reduction in gloss, distinctness of image, durability and weatherability. On the other hand, if a bake curing step is imposed between application of the base coat and clear coat layers to eliminate this problem, intercoat adherence may suffer.

There is thus a need in the art for acrylic-based resins which can be employed in base coat paint formulations, which can be readily dispersed and stabilized in water, and which are compatible with high solids, highly alkylated melamine type top coat formulations.

25 Summary of the Invention

The present invention provides, in its principal aspect, a water dilutable graft copolymer comprising the reaction product of A) an ethylenically terminated polyurethane macromonomer which is the reaction product of i) a polyisocyanate; ii) a compound having at least two functional groups reactive with isocyanate; 30 iii) a polyether having a single functional group reactive with isocyanate and a monoethylenically unsaturated monomer having a single functional group reactive with isocyanate; and B) one or more ethylenically unsaturated monomers. The copolymerization of these ethylenically unsaturated monomers form the backbone of the graft copolymer. Although different types of ethylenically unsaturated compounds may be used as discussed below, those most commonly employed are acrylic in nature and for convenience the backbone will sometimes be referred to herein as "acrylic" even though as noted above other types of ethylenically unsaturated monomer may have been employed.

In one particular embodiment the invention provides a stabilized water dilutable polyurethane graft copolymer comprising from 12 to 25% by weight of the the polyurethane macromonomer. In another aspect, there are provided pigmented base coat paint formulations suitable for application to metal and 40 plastic substrate bodies which comprise the above described polyurethane/acrylic graft copolymers. In yet another aspect of the present invention, there are provided substrate bodies coated with one or more base coat layers comprising the above-described polyurethane/acrylic graft copolymers.

Detailed Description

45 The resins of the present invention are graft copolymers comprising an acrylic backbone with pendant polyurethane graft side-chains which serve to solubilize and stabilize the copolymers in aqueous media. The resins are particularly adapted for use as both the principal binder resin and as the pigment grind resin in water-borne coating formulations. The resins of this invention combine the best features of sprayability of polyurethane resin compositions and the durability of acrylic resin compositions into a single resin system. By varying the composition and ratios of ethylenically unsaturated monomers in the acrylic backbone, the composition of the polyurethane graft side chains, and the ratio of polyurethane side-chain segments to acrylic backbone, design of the resin system of the present invention provides for a full range of structural variation for optimizing the resin system for a particular application.

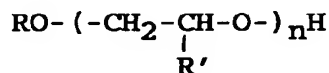
55 The resins of the present invention are formed by copolymerizing a mixture of monoethylenically unsaturated monomers and one or more polyurethane macromonomers which are terminated at one end with a polyether and at the other end with a monoethylenically unsaturated unit. The polyurethane macromonomers are prepared by reacting a mixture of a) a polyisocyanate; b) polyether having a single

functional group reactive with isocyanate such as an alkoxy poly(oxyalkylene) alcohol; c) a compound having at least two functional groups reactive with isocyanate such as a diol, triol, ester polyol, or mixture thereof; and d) a monethylenically unsaturated monomer which has a single functional group reactive with isocyanate.

5 The polyisocyanate which is employed to form the ethylenically-terminated polyurethane macromonomers of this invention is essentially any polyisocyanate, i.e. any compound containing at least two isocyanate functional groups. The polyisocyanate may be a triisocyanate such as 1,2,4-benzene triisocyanate, polymethylene polyphenyl isocyanate, or may be the trimerized isocyanurate of an alkyl diisocyanate such as the isocyanurate of 1,6-hexamethylene diisocyanate. The polyisocyanate is preferably
10 a diisocyanate, for example, hydrocarbon diisocyanates or substituted hydrocarbon diisocyanates. Examples of compounds which may be utilized include p-phenylene diisocyanate, biphenyl 4,4'-diisocyanate, meta-xylylene diisocyanate, toluene diisocyanate (TDI), 3,3'-dimethyl-4,4'-biphenylene diisocyanate, 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethylhexane-1,6-diisocyanate, 1,3-bis-[2-(2-(isocyanato)propyl)]benzene (also known as tetramethylxylyldiisocyanate, (TMXDI), methylene bis-
15 (phenyl isocyanate), 1,5-naphthalene diisocyanate, bis-(isocyanatoethyl fumarate), isophorone diisocyanate (IPDI), and methylene bis-(4-cyclohexylisocyanate). There can also be employed isocyanate-terminated adducts of diols such as ethylene glycol or 1,4-butylene glycol. These compounds are formed by reacting more than one mol of diisocyanate, such as those mentioned above, with one mol of diol to form a longer chain diisocyanate. Alternatively, the isocyanate-terminated diol adduct may be formed in situ by addition of
20 the diol together with the diisocyanate to the reaction mixture.

It is preferred to employ an aliphatic or cycloaliphatic diisocyanate or aliphatic isocyanurate since it has been found that these provide better color stability in the finished coating. Examples include 1,6-hexamethylene diisocyanate, the isocyanurate of 1,6-hexamethylene diisocyanate, 1,4-butylene diisocyanate, methylene bis-(4-cyclohexyl isocyanate), and isophorone diisocyanate (IPDI). However, aromatic diisocyanates in which the isocyanate groups are not directly attached to the aromatic ring such as
25 TMXDI and meta-xylylenediisocyanate may also be used.

The polyether having a single functional group reactive with isocyanate may be a polyether alcohol or polyether amine and is typically an alkoxy poly(oxyalkylene) alcohol oligomer formed by the alkoxyl-initiated polymerization of epoxides such as ethylene oxide and propylene oxide. The compounds have the general
30 formula



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where R is lower alkyl, R' is hydrogen or lower alkyl, and the nominal value of n ranges between 20 and 75. The compounds, when R is methyl and R' is hydrogen (formed by the methoxyl-initiated polymerization of ethylene oxide) are generally known as "MPEG's" (methoxy polyethylene glycols) and are commercially
40 available, for example, from Union Carbide Co. in a variety of molecular weights. The compounds are marketed under the tradenames MPEG XXXX where XXXX is a number indicating the average molecular weight. For the purposes of this invention, the preferred alkoxy poly(alkylene oxide) alcohols are the MPEG's having weight average molecular weights in the range of between 1200 and 3000. Particularly preferred are MPEG 1500 and MPEG 2000.

45 The compounds used in forming the polyurethane macromonomers of this invention are preferably aliphatic compounds, i.e. compounds having two or more hydroxyl functions per molecule and having a straight-chain, branched-chain, or saturated carbocyclic ring. Aliphatic diols and triols are believed to impart flexibility to the final copolymer. Examples include ethylene glycol, propylene glycol, butylene glycol, neopentyl glycol, trimethylolethane, 1,6 hexanediol trimethylolpropane, pentaerithrytol and similar diols and
50 triols of up to twenty carbon atoms.

Similarly, ester polyols formed by esterification of a diol or triol of the types just discussed with a carboxylic acid or hydroxy acid may also be used. These compounds are characterized by at least two hydroxy groups and one ester group per molecule. Examples include monoesters of diols such as ethylene glycol, propylene glycol, butylene glycol, 1,6-hexanediol, trimethylolethane, trimethylolpropane with hydroxy
55 acids or alkyl-substituted hydroxy acids. Examples include hydroxyacetic acid, hydroxypropionic acid and 3-hydroxy-2,2-dimethylpropanoic acid. A preferred ester polyol is the 3-hydroxy-2,2-dimethylpropyl ester of 3-hydroxy-2,2-dimethylpropanoic acid, commercially available as Esterdiol 204 from Union Carbide Company.

The monoethylenically unsaturated monomers having a single functional group reactive with isocyanate which are employed in the synthesis of the polyurethane macromonomers of this invention are preferably selected from hydroxyalkyl acrylates and methacrylates. Examples include hydroxymethyl acrylate, hydroxymethyl methacrylate, hydroxyethyl acrylate, hydroxyethyl methacrylate, hydroxypropyl acrylate, hydroxypropyl methacrylate, hydroxybutyl acrylate and hydroxybutyl methacrylate. 2-Hydroxyethyl acrylate is particularly preferred.

The polymers of this invention may be nonionically stabilized, or partially nonionically and partially anionically stabilized. The monoethylenically unsaturated monomers which are chosen to synthesize the acrylic backbone of the resins of this invention are chosen, based upon a decision to design a completely nonionically stabilized resin or a partially nonionically/partially anionically stabilized resin. In the case of completely nonionically stabilized polymers, the ethylenically unsaturated monomers chosen to fabricate the backbone of the resin are free of carboxyl group-containing monomers such as acrylic acid, methacrylic acid and fumaric acid. In this instance, the monomers for synthesis of the acrylic backbone are chosen from among the alkyl acrylates, alkyl methacrylates, hydroxyalkyl acrylates, hydroxyalkyl methacrylates and styrene with hydroxyalkyl acrylates and methacrylates predominating. The composition of the final polyurethane graft copolymer is then adjusted to contain a high degree of polar poly (oxylalkylene) segment in the polyurethane side-chain units to solubilize and stabilize the polymer in aqueous medium.

In the case of the partially nonionically and partially anionically stabilized graft copolymers of this invention, the ethylenically unsaturated monomers chosen to synthesize the backbone portion of the resins include small amounts of acrylic acid and/or methacrylic acid. Preferably, however, the amount of carboxyl group containing monomer (i.e. acrylic and/or methacrylic acid) is kept low.

In practice, the ratio of monomers employed in synthesizing the desired final polyurethane/acrylic graft polymer, including the ethylenically-terminated polyurethane macromonomer, is chosen so as to insure that the weight percent MPEG segment in the final polymer ranges between 5% and 25% by weight of the total resin, preferably between 10% and 15% by weight. The percentage of MPEG segment depends in turn on whether the desired product is to be totally nonionically or partially anionically stabilized. If the product is to be totally nonionically stabilized, the percentage of MPEG segment should be toward the high end of the stated percentage ranges, i.e. between 12% by weight to 25% by weight.

On the other hand, if a partially anionically stabilized resin product is desired, acrylic acid, methacrylic acid, or a mixture of the two are chosen to form a fraction of the monomer employed in synthesizing the backbone portion of the polymer, and the amount of MPEG segment in the polyurethane side-chain stabilizing groups may comprise less of the total final polymer, ranging at the lower ends of the ranges discussed above, generally between 5% and 15% by weight of the total final polyurethane/acrylic resin.

To prepare the ethylenically-terminated polyurethane macromonomers, the proportions of diisocyanate, hydroxyl functionalized monoethylenically unsaturated monomer, and diol and/or triol and nonionic stabilizer or monohydroxyfunctional polyether components are chosen so as to provide an alkoxy(polyoxyalkylene)-terminated and ethylenically-terminated macromonomer. This is accomplished by reacting a stoichiometric excess of the polyisocyanate, i.e. more than one isocyanate group per nucleophilic moiety (i.e. group reactive with isocyanate) in the other components with the hydroxyl functional group-containing reactants, i.e. diol, triol, ester diol, and alkoxy (polyoxyalkylene) alcohol in the presence of an antioxidant such as butylated hydroxy toluene. The preferred ratio of $-N=C=O$ functionality to hydroxyl functionality is chosen to be between 1.1 to 1.2.

The reaction is allowed to proceed until analysis of the reaction mixture indicates that an isocyanate functionality of 0.20 to 0.40 meq/g, preferably 0.25 remains. At this point, a capping agent is added and the reaction is allowed to proceed until all remaining isocyanate functionality has reacted. The capping agent may be a diol, triol or an amine polyol. Suitable diols for capping the free isocyanate functionality of the polyurethane macromonomer are straight-chain or branched chain aliphatic (i.e. saturated) diols or triols of from two to twenty carbon atoms. Examples include ethylene glycol, propylene glycol, butylene glycol, neopentyl glycol and 1,6-hexanediol. Straight-chain or branched-chain amino polyols of from two to twenty carbon atoms may also be employed as capping agents. By the term "amino polyol" as used throughout this specification and the appended claims is meant an organic compound having one primary or secondary amine nitrogen atom and one or more hydroxyl groups. Examples of amine polyols which may be used to cap the polyurethane macromonomers of this invention include ethanolamine, diethanolamine and 4-(2-hydroxyethyl)morpholine.

The weight average molecular weight of the polyurethane macromonomer is generally between 3,000 and 20,000 Daltons (5×10^{-21} g and 33.2×10^{-21} g), preferably between 6,000 and 13,000 Daltons.

The polyurethane macromonomer, thus prepared, is mixed with the blend of ethylenically unsaturated monomers which make up the acrylic backbone of the polymer and reacted in the presence of a suitable

free radical catalyst to form the resins of this invention. The ethylenically unsaturated monomers used are typically selected from acrylic and methacrylic acid, C₁₋₆ alkyl or hydroxyalkyl esters of such acids, C₁₋₆ alkyl or hydroxyalkyl esters of fumaric acid, styrene and vinyl toluene. The reaction is typically carried out under conditions of reflux in a suitably unreactive solvent such as toluene, xylene, or an alcohol such as n-butanol and iso-butanol. A free radical initiator is added to the reaction mixture together with the monoethylenically unsaturated monomers, and polyurethane macromonomer, with small amounts of catalyst added during later stages of the reaction if needed. Any suitable polymerization catalysts may be used to initiate copolymerization of the ethylenically unsaturated monomers and ethylenically-terminated polyurethane macromonomer including inorganic peroxy compounds such as potassium or ammonium persulfate, hydrogen peroxide or percarbonates; organic peroxy compounds such as acyl peroxides including, for example, benzoyl peroxide; alkyl hydroperoxides such as tert-butyl hydroperoxide, cumene hydroperoxide, and p-menthane hydroperoxide; dialkyl peroxides such as a di-tert-butyl peroxide; peroxy esters such as tert-butyl perbenzoate and tert-butyl peroctoate ; and mixtures thereof. The organic and inorganic peroxy compounds are advantageously used in combination with any suitable reducing agents known in the art, including sodium pyrosulfite or bisulfite, sodium formaldehyde sulfoxylate, triethanolamine and tetraethylene pentamine. Also azo compounds such as azo-bis-(iso-butyronitrile), azo-bis-(iso-butyric acid ethyl ester) and azi-bis-(iso-butyroamidine) may be employed as free radical initiators.

The initiator catalysts are employed in catalytic quantities normally used to initiate polymerization reactions of this type, i.e. generally in quantities of from 0.01% to 5% by weight, preferably between 0.02% and 1% by weight, based upon the total weight of ethylenically unsaturated monomer present in the reaction mixture.

As the reaction proceeds, the carbon-carbon double bond at the terminus of the monethylenically-terminated polyurethane macromonomer is incorporated into the growing acrylic backbone. The result is the formation of a polymer comprising preferably an acrylic backbone with pendant polyurethane graft side-chains. The polymerization reaction conditions are controlled to permit the formation of a graft copolymer of weight average molecular weight of between 15,000 and 60,000 Daltons, preferably between 25,000 and 40,000 Daltons.

The graft copolymers of this invention, prepared as described above can be employed as the principal or binder resin or as the pigment grind resin in base coat paint formulations for automotive applications. When employed as principal resins, the resins are combined, in amounts generally ranging between 10% by weight and about 40% by weight, based on total solids content of the base coat formulation, together with a pigment paste, a rheology control agent, leveling and flow additives, fillers, stabilizers, wetting agents, dispersing agents, adhesion promoters, etc. The pigment paste comprises a pigmenting agent (which may or may not additionally contain flake pigmenting agents such as aluminum flake, mica flake, or metal oxide encapsulated mica flake), and a pigment grind resin. The viscosity of the final base coat formulation is adjusted to the desired value by the addition of water.

Rheology control agents preferably incorporated into the base coat formulation help to control the viscosity of the resulting composition and are incorporated in amounts which prevent sagging or running after a base coat layer is sprayed onto a vertical substrate surface such as a motor vehicle body. The direct result of incorporating a rheology control agent is to provide flow control, body, and sprayability in the base coat formulation. Another favorable result of the inclusion of a rheology control agent is to allow for the application of thicker base coat layers during spraying, permitting better coverage and hiding of the substrate. The sprayed coatings containing these rheology control agents also exhibit better orientation of flake pigments such as aluminum or micaceous flakes which may be incorporated into the base coat formulation to provide a "metallic" sparkle effect.

Rheology control agents which can be used in embodiments of the present invention include fumed silica compounds, and hectorite and bentonite clays. Preferred fumed silica compounds are the hydrophobic fumed silicas such as Aerosil R972, available from Degussa Corporation, Frankfurt, West Germany). Another preferred rheology control agent for base coat compositions of the present invention is a synthetic sodium lithium magnesium silicate hectorite clay. An example of one such clay is Laponite RD, available from Laporte, Inc., Saddlebrook, NJ. The rheology control agent may also comprise mixtures of the above-mentioned agents.

The rheology control agent may comprise from 0% to 20% by weight of the basecoat composition, and generally comprises between 1% by weight and 5% by weight of the final base coat composition. In general, the particle size of the rheology control agent plays a role in the overall thixotropic properties of the base coat formulations. The rheology control agents included in embodiments of this invention are suspended in the formulations and are believed to function, at least in part, through coulombic or electrostatic interactions. In general, the particle size ranges from less than 0.01 μ m to over 200 μ m. The

particle size of the rheology control agent is selected to impart the desired flow, body, and sprayability of the finished base coat formulation. In most instances, the preferred particle size ranges between 1 μm and 10 μm .

Additional agents may also be included in the base coat formulations of this invention, for example
 5 surfactants, fillers, stabilizers, wetting agents, dispersing agents, adhesion promoters, etc. While agents serving each of these functions are well known in the art, the amounts used must be carefully controlled to avoid adversely affecting the coating and its drying characteristics.

When employed as a pigment grind resin, the polyurethane/acrylic graft copolymers of this invention are combined with one or more pigmenting agents known in the trade by conventional mixing, and then
 10 ground by ball milling, sand milling, passage through an attritor, or other known technique until the desired pigment particle size distribution is achieved. The paste is then diluted with water, if needed, to adjust the paste to the desired viscosity, and employed in base coat formulations as described above. In general, the resin will comprise from 30% by weight to 80% by weight of the total solids content of the pigment paste, preferably from 40% to 70% by weight.

The base coat compositions described hereinabove can be applied to a metal or plastic substrate in one or more coats using, for example, an air atomized spray gun such as a Binks Model 60 spray gun, available from the Sinks Manufacturing Corp., Franklen Park, IL, or by using other conventional spraying means. The base coat compositions are generally sprayed at a pressure of 50-80 psi (344.7-551.6 kPa), at a relative humidity of 50% to 90% (preferably 60% to 80%), and at temperatures between about 70-90 °F.
 15 (21.1-32.2 °C.).

After desposition of the base coat compositions, the base coat layer is flash dried at a temperature of between room temperature and about 145 °F. (62.8 °C.), preferably about 120 °F. (48.9 °C.). A second basecoat layer may be applied over the first without drying (flash off) or, alternatively, a clear coat layer may be desposited over the first flashed base coat layer. Any number of well known clear top coat
 25 compositions known in the art may be used to apply the top coat layer. For example a high solids solvent-borne top coat composition comprising a so-called monomeric highly alkylated melamine such as Cymel® 303 (available from American Cyanamid Company, Wayne, NJ) and a strong acid catalyst such as *p*-toluene sulfonic acid may be used. Alternatively, a top coat formulation utilizing a so-called polymeric less highly alkylated melamine such as Cymel® 327 may be used. As stated earlier, when a highly alkylated
 30 melamine resin is employed in the top coat formulation, it is preferred that the principal resin and grind resin of the bass coat formulation preferably be of the completely non-ionically stablized type free of carboxyl or carboxylate functionality When a polymeric less highly alkylated melamine resin is employed in the top coat formulation, the principal and/or grind resins of the base coat may be either the complete nonionically stabilized type in accordance with this invention or the partially anionically stabilized type. In
 35 this instance, the base coat principal or grind resins may also be a mixture of the completely nonionically stabilized (i.e. carboxyl or carboxylate functionality-free) type and the partially anionically stabilized (carboxyl or carboxylate functionality-containing) type.

After application of the clear coat layer over the previously applied base coat layer, the multi-layer coating is then baked to crosslink the polymeric vehicles and to drive the small amounts of water and
 40 organic solvents from the layers. A preferred baking step involves heating the coated substrate for a period of from about 10 to about 60 minutes at a temperature of between about 150 °F. (65.5 °C.) and 300 °F. (148.9 °C.). This baking step cures the multilayer coating to an attractive, glossy, hard, durable film.

The following examples are provided to enable one skilled in the art to practice the present invention.

45 Example 1

Preparation of Ethylenically-Terminated Polyurethane Macromonomer - I

A mixture of 953.4 grams of methoxy polyethylene glycol (MPEG 1500, available from Union Carbide),
 50 75 g of hydroxyethyl acrylate, 85.4 g of trimethylolpropane, 423.4 g of isophorone diisocyanate, 280 g of methyl propyl ketone and 10 g of butyl hydroxy toluene was placed in a 5-liter, three-necked flask fitted with a stirrer and condensor. The mixture was heated to about 85 °C. with stirring and held at that temperature until analysis indicated an isocyanate group functionality meq/g of 0.74. At that point, 5.5 g of dibutyl tin dilaurate was added to the reaction mixture and the mixture was further stirred and heated at 80-
 55 85 ° C. until analysis indicated an isocyanate group functionality meq/g of 0.33. Diethanolamine (66.3 g) was added to cap the residual isocyanate functionality, and the mixture stirred and heated until analysis indicated the absence of isocyanate functionality.

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The mixture was then cooled and 200 g of ethylene glycol monobutyl ether was added to the reaction mixture, followed a few minutes later by 4 g of butyl hydroxytoluene and then 200 g of deionized water. The mixture, 70% non-volatile content by weight, was filtered into a storage container for later use. The product resin contained 4.68% by weight hydroxyethyl acrylate and 59.46% methoxy polyethylene glycol based on the total weight of solids and was found to have a weight average molecular weight of about 7,000 Daltons ($11.62 \cdot 10^{-21}$ g) and a viscosity on the Gardner-Holt scale of Z1-Z2.

Example 2

10 Preparation of Ethylenically-Terminated Polyurethane Macromonomer - II

A mixture of the isocyanurate of hexamethylene diisocyanate (433 g, available as Desmodur N3390 from Mobay Chemical Corp., Plastics & Coatings Division, Pittsburgh, PA 15205), 36.4 g of neopentyl glycol, 1015 g of methoxy polyethylene glycol (MPEG 1500, available from Union Carbide), and 85 g of methyl propyl ketone were placed in a 5-liter flask fitted with a stirrer and condensor. The mixture was heated to 70 °C., at which point a mixture of 41.3 g of hydroxyethyl acrylate, 80 g of methyl propyl ketone, and 6 g of butyl hydroxy toluene were added to the flask contents. The temperature of the flask contents was raised to about 90 °C. and the flask contents were stirred and allowed to react at this temperature for a period of about three hours.

Five grams of a 3.3% by weight solution of dibutyl tin dilaurate in methyl propyl ketone were added to the flask contents, and the reaction was allowed to proceed at 90-95 °C. until analysis indicated an isocyanate function group meq/g of about 0.21. Diethanolamine (37 g) was added to cap the residual isocyanate functionality and the mixture was allowed to react at 90-95 °C. until analysis indicated the absence of isocyanate functionality. Ethylene glycol monobutyl ether (250 g) was added to the flask contents and the mixture allowed to cool to about 70 °C. At this point, 150 g of deionized water were added and the resulting mixture thoroughly mixed and filtered into a storage container for later use.

The product contained 71.5% non-volatiles and had a viscosity of U-V on the Gardner-Holt scale. The resin contained 66.4% methoxypolyethylene glycol and 2.7% hydroxyethyl acrylate, based on the total weight of solids, and had a weight average molecular weight of about 13,000. Daltons ($21.6 \cdot 10^{-21}$ g).

30 Example 3

Preparation of Ethylenically-Terminated Polyurethane Macromonomer - III

A mixture of isophorone diisocyanate (502.5 g), 123.0 g of trimethylolpropane, 25.5 g of the 3-hydroxy-2,2-dimethylpropylester of 3-hydroxy-2,2-dimethylpropanoic acid (available from Union Carbide as Esterdiol 204), 955 g of methoxy polyethylene glycol (available as MPEG 2000 from Union Carbide Co.), and 80 g of methyl propyl ketone was placed in a 5-liter flask fitted with a stirrer and condensor. The mixture was heated to 105 °C. and held, with stirring, at a temperature of between about 105 °C. and 110 °C. for a period of two hours. At the end of this time, the mixture was cooled to about 65 °C. and a mixture of 51 g of hydroxyethyl acrylate and 8.1 g of butyl hydroxytoluene in 100 g of methyl propyl ketone was added to the reaction mixture. After a few minutes, 3.4 g of a 3.3% weight percent solution of dibutyl tin dilaurate in methyl propyl ketone was added to the flask contents and the mixture was then stirred and held at a temperature of about 65 °C. to 70 °C. until analysis indicated an isocyanate group meq/g of about 0.33. Trimethylolpropane (86 g) was then added to the reaction mixture and heating at stirring at 65-70 °C. was continued until analysis indicated the absence of isocyanate functionality. The mixture was then cooled and 250 g of ethylene glycol monobutyl ether and 200 g of deionized water were added. The resulting product was 73% non-volatile solids, and had a viscosity of Z3-Z4 on the Gardner-Holt scale. The resin comprised 54.8% by weight methoxy polyethylene glycol and 2.93 % by weight hydroxy ethyl acrylate based on total solids, and had a weight average molecular weight of about 13,800 Daltons ($22.9 \cdot 10^{-21}$ g).

Example 4

Preparation of Ethylenically-Terminated Polyurethane Macromonomer - IV

A mixture of isophorone diisocyanate (488 g), 122.8 g of trimethylolpropane, 1040 g of methoxy polyethylene glycol (available as MPEG 2000 from Union Carbide Co.), and 100 g of methyl propyl ketone was placed in a 5-liter flask fitted with a stirrer and condensor. The mixture was heated to 105 °C. and held,

with stirring, at a temperature of between about 105 °C. and 110 °C. for a period of two hours. At the end of this time, the mixture was cooled to about 68 °C. and a mixture of 56.6 g of hydroxyethyl acrylate and 8.5 g of butyl hydroxytoluene in 85 g of methyl propyl ketone was added to the reaction mixture. After a few minutes, 4.0 g of a 3.3% weight percent solution of dibutyl tin dilaurate in methyl propyl ketone was added to the flask contents and the mixture was then stirred and held at a temperature of about 65 °C. to 70 °C. until analysis indicated an isocyanate group meq/g of about 0.34. 1,6-Hexanediol (77.3 g) was then added to the reaction mixture and heating at stirring at 65-70 °C. was continued until analysis indicated the absence of isocyanate functionality. The mixture was then cooled and a mixture of 259 g of ethylene glycol monobutyl ether and 3 g of butyl hydroxytoluene was added, followed by 200 g of deionized water. The resulting product was 73% non-volatile solids, and had a viscosity of Z1-Z2 on the Gardner-Holt scale. The resin comprised 58.3% by weight methoxy polyethylene glycol and 4.34% by weight hydroxy ethyl acrylate based on total solids, and had a weight average molecular weight of about 13,500 Daltons ($22.4 \cdot 10^{-21}$ g).

Example 5

Preparation of Polyurethane/Acrylic Graft Copolymer I

A 5-liter three-neck flask was equipped with a stirrer, condensor, and addition funnel. A mixture of 150 g of methyl propyl ketone and 250 g of ethylene glycol monobutyl ether was charged to the flask and the mixture heated to reflux (about 108 °C.).

A mixture was prepared of 400 g of the ethylenically terminated polyurethane macromonomer from Example 1, 170 g of methyl methacrylate, 300 g of butyl acrylate, 250 g of hydroxyethyl acrylate, and 76 g of *tert*-butyl peroxoate. This mixture was added gradually to the refluxing flask contents over a period of about four hours. When addition was complete, the resulting mixture was allowed to react for an additional one-half hour after which time an additional 10 g of *tert*-butyl peroxoate, dissolved in 30 g of ethylene glycol monobutyl ether, was added to the flask. The mixture was allowed to react under reflux for an additional one-half hour, after which time the flask contents were cooled and 1800 g of deionized water was added with vigorous stirring.

The product mixture was a clear solution, having 30% non-volatile solids content and a viscosity of about 3 Pas (3000 centipoises) and a pH of 4. The product resin had a calculated T_g of -15 °C., 16.6% by weight MPEG stabilizer content (based on total solids), 25% by weight hydroxyethyl acrylate content (based on total solids), and a weight average molecular weight of 24,500 Daltons ($40.7 \cdot 10^{-21}$ g).

Example 6

Preparation of Polyurethane/Acrylic Graft Copolymer II

A 5-liter three-neck flask was equipped with a stirrer, condensor, and addition funnel. *n*-Butanol (275 g) was charged to the flask and heated to reflux.

A mixture was prepared of 425 g of the ethylenically terminated polyurethane macromonomer from Example 2, 150 g of hydroxyethyl acrylate, 120 g of 2-ethylhexyl acrylate, 480 g of butyl acrylate, and 25 g of *tert*-butyl peroxoate in 75 g of *D*-butanol. This mixture was added gradually to the flask contents under reflux (about 110-115 °C.) over a period of about four hours. When addition was complete, the mixture was heated under reflux for an additional one-half hour and then cooled. Deionized water (2000 g) was added, and the clear product dispersion was filtered into a container and stored for later use.

The product mixture was a clear dispersion, having 30% non-volatile solids content and a viscosity of about 3500 centipoises and a pH of 5.9. The product resin had a calculated T_g of -6 °C., 20% by weight MPEG content (based on total solids), 15% by weight hydroxyethyl acrylate content (based on total solids), and a weight average molecular weight of 25,000 Daltons ($41.5 \cdot 10^{-21}$ g).

Example 7

Preparation of Polyurethane/Acrylic Graft Copolymer III

A 5-liter three-neck flask was equipped with a stirrer, condensor, and addition funnel. *n*-Butanol (410 g) was charged to the flask and heated to reflux.

A mixture was prepared of 238 g of the ethylenically terminated polyurethane macromonomer from Example 3, 350 g of hydroxyethyl acrylate, 179.9 g of 2-ethylhexyl acrylate, 296.7 g of methyl methacrylate,

and 12.4 g of *tert*-butyl peroctoate. This mixture was added gradually to the flask contents under reflux (about 110-118°C.) over a period of about four hours. When addition was complete, 5.7 g of *tert*-butyl peroctoate in g of *n*-butanol was added to the flask and heating was continued for an addition one-half hour. At the end of this time, the mixture was cooled and 2000 g of deionized water was added to the flask contents with vigorous stirring. The product was filtered into a storage container for later use.

The clear product dispersion had a dispersion particle size of 105 nanometers, 30% non-volatile solids content, a viscosity of about 2.3 Pas (2300 centipoises) and a pH of 4.2. The product resin had a calculated T_g of -6°C., 20% by weight MPEG content (based on total solids), 15% by weight hydroxyethyl acrylate content (based on total solids), and a weight average molecular weight of 25,000 Daltons ($41.5 \cdot 10^{-21}$ g).

Example 8

Preparation of Polyurethane/Acrylic Graft Copolymer IV

A 5-liter three-neck flask was equipped with a stirrer, condensor, and addition funnel. *n*-Butanol (430 g) was charged to the flask and heated to reflux.

A mixture was prepared of 209.5 g of the ethylenically terminated polyurethane macomonomer from Example 4, 400 g of hydroxyethyl acrylate, 155 g of 2-ethylhexyl acrylate, 293 g of methyl methacrylate, and 18 g of *tert*-butyl peroctoate. This mixture was added gradually to the flask contents under reflux (about 110-118°C.) over a period of about four hours. When addition was complete, the mixture was heated under reflux for an additional one-half hour, at which point 5 g of *tert*-butyl peroctoate in 35 g of *n*-butanol was added to the flask and heating was continued for an additional one-half hour. At the end of this time, the mixture was cooled and 1900 g of deionized water was added to the flask contents with vigorous stirring. The product was filtered into a storage container for later use.

The clear product dispersion had a dispersion particle size of 150 nanometers, 29% non-volatile solids content, a viscosity of about 3.3 Pas (3300 centipoises) and a pH of 4.4. The product resin comprised 8.9% by weight MPEG content (based on total solids), 40% by weight hydroxyethyl acrylate content (based on total solids), and a weight average molecular weight of 28,000 Daltons ($46.5 \cdot 10^{-21}$ g).

Example 9

Preparation of Polyurethane/Acrylic Graft Copolymer V

A 5-liter three-neck flask was equipped with a stirrer, condensor, and addition funnel. *n*-Butanol (410 g) was charged to the flask and heated to reflux.

A mixture was prepared of 145.7 g of the ethylenically terminated polyurethane macomonomer from Example 3, 360 g of hydroxyethyl acrylate, 203 g of 2-ethylhexyl acrylate, 312 g of methyl methacrylate, 19 g of acrylic acid, and 15.5 g of *tert*-butyl peroctoate. This mixture was added gradually to the flask contents under reflux (about 110-118°C.) over a period of about four hours. When addition was complete, the mixture was heated under reflux for an additional one-half hour, at which point 5 g of *tert*-butyl peroctoate in 35 g of *n*-butanol was added to the flask and heating was continued for an additional one-half hour. At the end of this time, the mixture was cooled and 29 g of 4-ethylmorpholine was added to the flask contents with stirring to neutralize the carboxyl functionality. Following this, 1900 g of deionized water was added to the flask contents with vigorous stirring. The product was filtered into a storage container for later use.

The clear product dispersion had a dispersion particle size of 135 nanometers, 30% non-volatile solids content, a viscosity of about 3.7 Pas (3700 centipoises), an acid number of 15 based on total solids, and a pH of 7.5. The product resin had a calculated theoretical T_g of 0°C., comprised 15% by weight MPEG content (based on total solids), and had a weight average molecular weight of 32,100 Daltons ($53.3 \cdot 10^{-21}$ g).

Example 10

Preparation of Polyurethane/Acrylic Graft Copolymer VI

A 5-liter three-neck flask was equipped with a stirrer, condensor, and addition funnel. *n*-Butanol (415 g) was charged to the flask and heated to reflux.

A mixture was prepared of 249.8 g of the ethylenically terminated polyurethane macomonomer from Example 3, 400 g of hydroxyethyl acrylate, 149.8 g of 2-ethylhexyl acrylate, 255.1 g of methyl methacrylate,

13.3 g of acrylic acid, and 18.2 g of *tert*-butyl peroctoate. This mixture was added gradually to the flask contents under reflux (about 110-118 °C.) over a period of about four hours. When addition was complete, the mixture was heated under reflux for an additional one-half hour, at which point 5 g of *tert*-butyl peroctoate in 30 g of *n*-butanol was added to the flask and heating was continued for an additional one-half hour. At the end of this time, the mixture was cooled and 16.4 g of dimethylethanolamine was added to the flask contents with stirring to neutralize the carboxyl functionality. Following this, 1700 g of deionized water was added to the flask contents with vigorous stirring. The product was filtered into a storage container for later use.

The clear product dispersion had a dispersion particle size of 70 nanometers, 31% non-volatile solids content, a viscosity of about 5 Pas (5000 centipoises), an acid number of 10.5 based on total solids, and a pH of 7.85. The product resin had a calculated theoretical T_g of 0 °C., comprised 10% by weight MPEG content (based on total solids), and had a weight average molecular weight of 43,000 Daltons ($71.4 \cdot 10^{-21}$ g).

Example 11

Preparation of a Water-Borne Silver Base Coat

A series of silver base coat paint formulations were prepared using the polyurethane/acrylic graft polymers prepared as described above in Examples 5 through 10. In each case, a pigment slurry was prepared by thoroughly blending 1450.2 g of aluminum pigment (60% solids) with 1633.8 g of partially methylated melamine (90% active) and 415.2 g of ethylene glucol monobutyl ether. This slurry was then thoroughly blended with the principal resin dispersion of each Example in accordance with the formulations given in Table 1.

Following complete mixing of the aluminum pigment slurry and principal resin dispersion, the rheology control agent was blended into the mixture with high speed mixing. Deionized water was then added to the mixture until the non-volatile content was reduced to about 20% by weight and a viscosity of about 30 seconds in a #2 Fisher cup was achieved.

Table 1
Base Coat Formulations

| Ingredients | Example 12 | Example 13 | Example 14 | Example 15 | Example 16 | Example 17 |
|--|------------|------------|------------|------------|------------|------------|
| Aluminum pigment slurry | 583.2 | 583.2 | 583.2 | 583.2 | 583.2 | 583.2 |
| Principal resin dispersion of Example 5 | 1906.0 | --- | --- | --- | --- | --- |
| Principal resin dispersion of Example 6 | --- | 1906.0 | --- | --- | --- | --- |
| Principal resin dispersion of Example 7 | --- | --- | 1906.0 | --- | --- | --- |
| Principal resin dispersion of Example 8 | --- | --- | --- | 1918.0 | --- | --- |
| Principal resin dispersion of Example 9 | --- | --- | --- | --- | 1906.0 | --- |
| Principal resin dispersion of Example 10 | --- | --- | --- | --- | --- | 1845.0 |
| Rheology control agent 2% aqueous dispersion of Laponite RD [®] | 1650.0 | 1650.0 | 1650.0 | 1650.0 | 1650.0 | 1650.0 |

Example 18

Preparation of Red Pigment Paste

The polyurethane/acrylic graft copolymer (82.35 g), prepared as described above in Example 9, was thoroughly mixed over a period of about one-half hour, with 12.9 g of C.I. Pigment Red 202 (available as Magenta B RT-343-D from Ciba-Geigy Corp., Three Skyline Drive, Hawthorne, NY 10532). This mixture was diluted by the addition of 4.75 g of deionized water and again mixed. This mixture had a viscosity of 66 Krebs units, and had a pH of 7.8.

An attritor was loaded with 1/8" steel media and charged with the above mixture. After 3 hours, the pigment particle size was found to be about 6 microns on the Hegman scale, and the suspension had a viscosity of 68 Krebs units and a pH of 7.8. The mixture contained 20.59% by weight polyurethane/acrylic graft copolymer and 1.90% by weight pigment, based on total solids.

Testing

Each base coat formulation of Examples 12 through 17 was hand sprayed over an electrocoated cold rolled steel panel at 80 °F. (26.7 °C.) at 60% relative humidity. Two sets of panels were prepared. In one set, the base coat was applied, flash dried, and overcoated with a clear coat layer, with both layers being subsequently bake cured. In the other set, only a base coat layer was applied prior to the bake curing step. In the case of panels which received a subsequent clear coat layer, following application of the base coat, each panel was placed in an oven at 110 °F. (43.3 °C.) for five minutes to flash dry the base coat layer. A layer of high solids clear coat containing a highly alkylated melamine (Cymel® 303, available from American Cyanamid Co., Wayne, NJ 07470) was then spray applied over the uncured base coat layer. The double-coated panels were then placed in an oven at 250 °F. (121 °C.) for thirty minutes to cure both layers. In the case of the panels which did not receive a clear top coat layer, the panels were bake cured at 250 °F. (121 °C.) following spray application of the base coat layer.

The panels which had received a base coat layer only were subjected to a solvent rub test and the results compared with similarly prepared panels which had received a base coat layer prepared from a polyurethane principal resin of the type disclosed in United States Patent 4,794,147. In this test, a soft cloth was saturated with methyl ethyl ketone and the cloth was then rubbed in a back-and-forth motion over the coated panel until there was evidence of softening or removal of the baked base coat layer. In this test, the prior art polyurethane base coat layer showed softening or failure after ten to fifteen rubs, while the panels coated with the polyurethane/acrylic graft resin coatings of the present invention did not show any softening before fifty to one-hundred rubs.

In another test, the panels which had received both a base coat layer in accordance with this invention and a clear coat layer were subjected to conditions of 100% relative humidity and 100 °F. (37.8 °C.) temperature for a period of ten days. After this treatment, each of the panels was scribed with an awl to produce a large "X" on the panel, cutting through the coating layers to the bare substrate metal. A piece of adhesive tape is pressed over the scribe mark, and pulled away. Removal of any of the coating layers is considered adhesive failure. The results of the adhesion tape-pull tests are given in Table 2.

Table 2

| Example | Results of Adhesion Tape-Pull Test |
|---------|------------------------------------|
| 12 | Pass |
| 13 | Pass |
| 14 | Pass |
| 15 | Pass |
| 16 | Pass |
| 17 | Pass |

As discussed above, the use of an amine-solubilized base coat formulation with a high solids type clear coat formulation often causes problems. Amines, freed from the basecoat layer during the bake curing step will partially neutralize the strong acid catalyst required for curing of the monomeric fully alkylated melamine cross-linking resins contained in a high solids clear top coat. The result is severe loss of "distinctness of image" or DOI. DOI is the glossiness of the topcoat, and can be measured, in one

technique, by the use of ASTM 4449-85 in which the scattering of light at the edges of a specularly reflected beam of light from the top coat surface is measured.

The DOI of panels coated with the formulations of Examples 12-17 and overcoated with a super high solids acrylic clear coat cross-linked with a monomeric fully alkylated melamine resin appear in Table 3, compared with a panel which had been coated with a prior art anionic polyurethane basecoat and the same top coat formulation. In addition, Table 3 shows the DOI values for panels coated with the basecoat formulations of Examples 12-17 and overcoated with a high solids acrylic clear coat using a polymeric partially alkylated melamine cross-linking agent.

Table 3

| Base Coat of Example | Clear Coat Type | DOI |
|--------------------------------|---|-----|
| 12 | High-solids acrylic, monomeric highly alkylated melamine cross-linker | 85 |
| 13 | Ditto | 83 |
| 14 | Ditto | 86 |
| 15 | Ditto | 85 |
| Prior art anionic polyurethane | Ditto | 5 |
| 12 | High-solids acrylic, polymeric, partially alkylated melamine cross-linker | 83 |
| 13 | Ditto | 85 |
| 14 | Ditto | 85 |
| 15 | Ditto | 86 |
| Prior art anionic polyurethane | Ditto | 85 |

As can be seen by examining the data in Table 3, when a high solids acrylic top coat formulation, employing a monomeric highly alkylated melamine cross-linking agent, is applied over the base coat formulations of the present invention, good gloss and distinctness of image is maintained for the resulting multi-layer coating. In contrast, when a typical prior art water-borne polyurethane base coat formulation, solubilized by amine, is employed with the same top coat, considerable loss in distinctness of image occurs. That this result is due to interference with amine (derived from the base coat layer) with the strong acid catalyst in the top coat can be seen by examining the data in the last half of Table 3. There, a high-solids acrylic top coat formulation which is cross-linked with a polymeric partially-alkylated melamine cross-linking agent which does not require strong acid catalysts for cross-linking. The gloss and distinctness of image for both the coatings of this invention and for the prior art amine-solubilized polyurethane coatings is good.

Claims

1. A water dilutable graft copolymer comprising the reaction product of:
 - A) an ethylenically terminated polyurethane macromonomer which is the reaction product of
 - i) a polyisocyanate;
 - ii) a compound having at least two functional groups reactive with isocyanate;
 - iii) a polyether having a single functional group reactive with isocyanate; and
 - iv) a monoethylenically unsaturated monomer having a single functional group reactive with isocyanate
 - B) one or more ethylenically unsaturated monomers.
2. A graft copolymer as defined by claim 1, further reacted with a capping agent.
3. A graft copolymer as defined by claim 2, wherein said capping agent is selected from diols, triols, aminopolyols, and mixtures thereof.
4. A graft copolymer as defined by claim 3, wherein said capping agent is selected from straight chain and branched chain diols of from two to twenty carbon atoms, preferably propylene glycol, butylene glycol, neopentyl glycol, or 1,6-hexanediol, or is a straight chain or branched chain aliphatic triol of from three to twenty carbon atoms or a mixture thereof, preferably trimethylolethane, trimethylolpropane,

pentaerythritol or a mixture of two or more thereof or is an amino polyol of from two to twenty carbon atoms, preferably aminoethanol or diethanolamine.

- 5 5. A graft copolymer as defined by any one of the preceding claims, having a weight average molecular weight between 15,000 Daltons and 60,000 Daltons (24.9×10^{-21} g and 99.6×10^{-21} g).
- 10 6. A graft copolymer as defined by any one of the preceding claims, wherein said compound having at least two functional groups reactive with isocyanate is selected from the group consisting of ester polyols, diols, triols, and mixtures thereof.
- 15 7. A graft copolymer as defined by claim 6, wherein said compound having at least two functional groups reactive with isocyanate is selected from straight chain and branched chain aliphatic diols of from two to twenty carbon atoms and mixtures thereof, preferably selected from ethylene glycol, propylene glycol, butylene glycol, neopentyl glycol, 1,6-hexanediol and mixtures thereof, or is selected from the group consisting of straight chain and branched chain aliphatic triols of from three to twenty carbon atoms and mixtures thereof, preferably selected from trimethylolethane, trimethylolpropane, and pentaerythritol and mixtures thereof, or is selected from polyester polyols of from four to twenty carbon atoms, preferably the 3-hydroxy-2,2-dimethylpropyl ester of 3-hydroxy-2,2-dimethylpropanoic acid.
- 20 8. A graft copolymer as defined by any one of the preceding claims, wherein said polyisocyanate is selected from aliphatic polyisocyanates, cycloaliphatic polyisocyanates, aliphatic isocyanurates, and mixtures thereof and is preferably selected from 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethylhexane-1,6-diisocyanate, 1,3-bis-[2-(2-(isocyanato) propyl)]benzene (TMXDI), meta-xylylene diisocyanate, bis-(isocyanatoethyl fumarate), isophorone diisocyanate (IPDI), and methylene bis-(4-cyclohexylisocyanate).
- 25 9. A graft copolymer as defined by any one of the preceding claims, wherein said ethylenically unsaturated monomers are selected from the group consisting of acrylic acid, methacrylic acid,
 - 30 C₁-C₆ alkyl esters of acrylic acid,
 - C₁-C₆ alkyl esters of methacrylic acid,
 - C₁-C₆ hydroxyalkyl esters of acrylic acid,
 - C₁-C₆ hydroxyalkyl esters of methacrylic acid,
 - C₁-C₆ alkyl esters of fumaric acid,
 - 35 C₁-C₆ hydroxyalkyl esters of fumaric acid,
 - styrene, and
 - vinyltoluene.
- 40 10. A graft copolymer as defined by any one of the preceding claims, wherein said polyether is selected from polyether alcohols and polyether amines and is preferably selected from the group consisting of polyether alcohols having a weight average molecular weight between 1200 and 3000 Daltons ($2 \cdot 10^{-21}$ g and $5 \cdot 10^{-21}$ g).
- 45 11. A graft copolymer as defined by any one of the preceding claims, wherein said ethylenically terminated polyurethane macromonomer has a weight average molecular weight of between about 3,000 Daltons and 20,000 Daltons (5×10^{-21} g and 33.2×10^{-21} g).
- 50 12. A graft copolymer as defined by claim 10, wherein said graft copolymer contains between 5% and 25% by weight of said polyether alcohols.
- 55 13. A stabilized, water dilutable graft copolymer as defined by claim 1 comprising the reaction product of:
 - A) from 12% by weight to 25 % by weight of an ethylenically terminated polyurethane macromonomer which is the reaction product of
 - i) a polyisocyanate;
 - ii) a compound having at least two functional groups reactive with isocyanate;
 - iii) a polyether having a single functional group reactive with isocyanate; and
 - iv) a monoethylenically unsaturated monomer having a single functional group reactive with isocyanate

- B) one or more ethylenically unsaturated monomers selected from the group consisting of
 C₁-C₆ alkyl esters of acrylic acid,
 C₁-C₆ alkyl esters of methacrylic acid,
 C₁-C₆ hydroxyalkyl esters of acrylic acid,
 C₁-C₆ hydroxyalkyl esters of methacrylic acid,
 C₁-C₆ alkyl esters of fumaric acid,
 C₁-C₆ hydroxyalkyl esters of fumaric acid,
 styrene, vinyltoluene, acrylic acid, and methacrylic acid.
14. A pigment paste comprising between 30% by weight and 80% by weight of a water dilutable graft copolymer as defined by any one of the preceding claims and one or more pigmenting agents.
15. A substrate body coated with one or more base layers of a coating composition comprising a water-dilutable graft copolymer as defined by any one of claims 1-13.

Patentansprüche

1. Mit Wasser verdünnungsfähiges Pfpfocopolymer, umfassend das Reaktionsprodukt:
 (A) ein ethylenisch terminiertes Polyurethan-Makromonomer als das Reaktionsprodukt von:
 (i) einem Polyisocyanat;
 (ii) einer Verbindung mit mindestens zwei mit Isocyanat reaktionsfähigen, funktionalen Gruppen;
 (iii) einem Polyether mit einer einzelnen mit Isocyanat reaktionsfähigen, funktionalen Gruppe; und
 (iv) einem monoethylenisch ungesättigtem Monomer mit einer einzelnen mit Isocyanat reaktionsfähigen, funktionalen Gruppe;
 (B) einem oder mehreren ethylenisch ungesättigten Monomeren.
2. Pfpfocopolymer nach Anspruch 1, ferner umgesetzt mit einem Terminierungsmittel.
3. Pfpfocopolymer nach Anspruch 2, bei welchem das Terminierungsmittel ausgewählt wird aus Diolen, Triolen, Aminopolyolen und deren Mischungen.
4. Pfpfocopolymer nach Anspruch 4, bei welchem das Terminierungsmittel ausgewählt wird aus geradkettigen und verzweigt-kettigen Diolen mit zwei bis zwanzig Kohlenstoffatomen, vorzugsweise Propylenglykol, Butylenglykol, Neopentylglykol oder 1,6-Hexandiol, oder ausgewählt wird aus geradkettigem und verzweigt-kettigem aliphatischem Triol mit drei bis Zwanzig Kohlenstoffatomen oder deren Mischungen, vorzugsweise Trimethylolethan, Trimethylolpropan, Pentaerythrit oder einer Mischung von zwei oder mehreren davon, oder ein Aminopolyol mit zwei bis zwanzig Kohlenstoffatomen ist, vorzugsweise Aminoethanol oder Diethanolamin.
5. Pfpfocopolymer nach einem der vorstehenden Ansprüche mit einer massegemittelten Molekülmasse zwischen 15.000 Dalton und 60.000 Dalton ($24,9 \times 10^{-21}$ g bzw. $99,6 \times 10^{-21}$ g).
6. Pfpfocopolymer nach einem der vorstehenden Ansprüche, bei welchem die mit Isocyanat reaktionsfähige Verbindung mit mindestens zwei funktionalen Gruppen ausgewählt wird aus der Gruppe, bestehend aus Esterpolyolen, Diolen, Triolen und deren Mischungen.
7. Pfpfocopolymer nach Anspruch 6, bei welchem die mit Isocyanat reaktionsfähige Verbindung mit mindestens zwei funktionalen Gruppen ausgewählt wird aus geradkettigem und verzweigt-kettigen aliphatischen Diolen mit zwei bis zwanzig Kohlenstoffatomen oder deren Mischungen, vorzugsweise ausgewählt aus Ethylenglykol, Propylenglykol, Butylenglykol, Neopentylglykol oder 1,6-Hexandiol und deren Mischungen, oder ausgewählt wird aus geradkettigen und verzweigt-kettigen aliphatischen Triolen mit drei bis zwanzig Kohlenstoffatomen und deren Mischungen, vorzugsweise ausgewählt aus Trimethylolethan, Trimethylolpropan, Pentaerythrit und Mischungen davon, oder ausgewählt wird aus Polyesterpolyolen mit vier bis zwanzig Kohlenstoffatomen, vorzugsweise der 3-Hydroxy-2,2-dimethylpropylester der 3-Hydroxy-2,2-dimethylpropansäure.
8. Pfpfocopolymer nach einem der vorstehenden Ansprüche, bei welchem das Polyisocyanat ausgewählt wird aus aliphatischen Polyisocyanaten, cycloaliphatischen Polyisocyanaten, aliphatischen Isocyanura-

ten und Mischungen davon, und vorzugsweise ausgewählt wird aus 1,4-Tetramethyldiisocyanat, 1,6-Hexamethyldiisocyanat, 2,2,4-Trimethylhexan-1,6-diisocyanat, 1,3-Bis-[2-(2-(isocyanato)propyl)]benzol (TMXDI), m-Xyloldiisocyanat, Bis-(isocyanatoethylfumarat), Isophorondiisocyanat (IPDI) und Methylenbis-(4-cyclohexyldiisocyanat).

5

9. Pfcopolymer nach einem der vorstehenden Ansprüche, bei welchem die ethylenisch ungesättigten Monomere ausgewählt werden aus der Gruppe, bestehend aus:

Acrylsäure

Methacrylsäure

10

C₁...C₆-Alkylester der Acrylsäure

C₁...C₆-Alkylester der Methacrylsäure

C₁...C₆-Hydroxyalkylester der Acrylsäure

C₁...C₆-Hydroxyalkylester der Methacrylsäure

C₁...C₆-Alkylester der Fumarsäure

15

C₁...C₆-Hydroxyalkylester der Fumarsäure

Styrol sowie

Vinyltoluol.

10. Pfcopolymer nach einem der vorstehenden Ansprüche, bei welchem der Polyether ausgewählt wird aus Polyetheralkoholen, Polyetheraminen und vorzugsweise ausgewählt wird aus der Gruppe, bestehend aus Polyetheralkoholen mit einer massegemittelten Molekülmasse zwischen 1.200 und 3.000 Dalton (1×10^{-21} g bzw. 5×10^{-21} g).

11. Pfcopolymer nach einem der vorstehenden Ansprüche, bei welchem das ethylenisch terminierte Polyurethan-Makromonomer eine massegemittelte Molekülmasse zwischen 3.000 Dalton und 20.000 Dalton (5×10^{-21} g bzw. $32,2 \times 10^{-21}$ g) hat.

12. Pfcopolymer nach Anspruch 10, bei welchem das Pfcopolymer zwischen 5 % ... 25 Gewichtsprozent der Polyetheralkohole enthält.

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13. Stabilisiertes, mit Wasser verdünnungsfähiges Pfcopolymer nach Anspruch 1, umfassend das Reaktionsprodukt von:

(A) 12 % ... 25 Gewichtsprozent ethylenisch terminiertes Polyurethan-Makromonomer als das Reaktionsprodukt von:

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(i) einem Polyisocyanat;

(ii) einer Verbindung mit mindestens zwei mit Isocyanat reaktionsfähigen, funktionalen Gruppen;

(iii) einem Polyether mit einer einzelnen mit Isocyanat reaktionsfähigen, funktionalen Gruppe; und

(iv) einem monoethylenisch ungesättigten Monomer mit einer einzelnen mit Isocyanat reaktionsfähigen, funktionalen Gruppe;

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(B) einem oder mehreren ethylenisch ungesättigten Monomeren ausgewählt aus der Gruppe, bestehend aus

C₁...C₆-Alkylester der Acrylsäure

C₁...C₆-Alkylester der Methacrylsäure

C₁...C₆-Hydroxyalkylester der Acrylsäure

45

C₁...C₆-Hydroxyalkylester der Methacrylsäure

C₁...C₆-Alkylester der Fumarsäure

C₁...C₆-Hydroxyalkylester der Fumarsäure

Styrol

Vinyltoluol

50

Acrylsäure

Methacrylsäure.

14. Pigmentpaste, umfassend zwischen 30 % ... 80 Gewichtsprozent mit Wasser verdünnungsfähiges Pfcopolymer nach einem der vorstehenden Ansprüche und ein oder mehrere Pigmentierungsmittel.

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15. Substratkörper, beschichtet mit einer oder mehreren Grundschichten einer Beschichtungszusammensetzung, umfassend ein mit Wasser verdünnungsfähiges Pfcopolymer nach einem der Ansprüche 1 bis 13.

Revendications

1. Copolymère greffé pouvant être dilué dans l'eau, comprenant le produit réactionnel :
 - A) d'un macromonomère de polyuréthane à terminaison éthylénique qui est le produit réactionnel
 - i) d'un polyisocyanate,
 - ii) d'un composé ayant au moins deux groupements fonctionnels réactifs avec un isocyanate,
 - iii) d'un polyéther ayant un seul groupement fonctionnel réactif avec un isocyanate et
 - iv) d'un monomère monoéthyléniquement insaturé ayant un seul groupement fonctionnel réactif avec un isocyanate;
 - B) d'un ou plusieurs monomères éthyléniquement insaturés.
2. Copolymère greffé selon la revendication 1, ayant réagi de plus avec un agent bloquant.
3. Copolymère greffé selon la revendication 2, dans lequel on choisit ledit agent bloquant parmi les diols, les triols, les aminopolyols et leurs mélanges.
4. Copolymère greffé selon la revendication 3, dans lequel on choisit ledit agent bloquant parmi les diols à chaîne linéaire et ramifiée ayant de 2 à 20 atomes de carbone, de préférence parmi le propylèneglycol, le butylèneglycol, le néopentylglycol ou le 1,6-hexanediol, ou bien l'agent est un triol aliphatique à chaîne linéaire ou ramifiée ayant de 3 à 20 atomes de carbone ou un de ses mélanges, de préférence le triméthyloléthane, le triméthylolpropane, le pentaérythritol ou un mélange de deux ou plusieurs d'entre eux, ou bien il est un aminopolyol ayant de 2 à 20 atomes de carbone, de préférence l'aminoéthanol ou la diéthanolamine.
5. Copolymère greffé selon l'une quelconque des revendications précédentes, ayant une masse moléculaire moyenne en masse comprise entre 15 000 d et 60 000 d ($24,9 \times 10^{-21}$ g et $99,6 \times 10^{-21}$ g).
6. Copolymère greffé selon l'une quelconque des revendications précédentes, dans lequel on choisit ledit composé ayant au moins deux groupements fonctionnels réactifs avec un isocyanate dans le groupe constitué des esterpolyols, des diols, des triols et de leurs mélanges.
7. Copolymère greffé selon la revendication 6, dans lequel on choisit ledit composé ayant au moins deux groupements fonctionnels réactifs avec un isocyanate parmi les diols aliphatiques à chaîne linéaire et ramifiée ayant de 2 à 20 atomes de carbone et leurs mélanges, de préférence parmi l'éthylèneglycol, le propylèneglycol, le butylèneglycol, le néopentylglycol, le 1,6-hexanediol et leurs mélanges, ou bien on le choisit dans le groupe constitué des triols aliphatiques à chaîne linéaire et ramifiée ayant de 3 à 20 atomes de carbone et leurs mélanges, de préférence parmi le triméthyloléthane, le triméthylolpropane et le pentaérythritol et leurs mélanges, ou bien encore parmi les polyesterpolyols ayant de 4 à 20 atomes de carbone, de préférence parmi l'ester 3-hydroxy-2,2-diméthylpropylique d'acide 3-hydroxy-2,2-diméthylpropanoïque.
8. Copolymère greffé selon l'une quelconque des revendications précédentes, dans lequel on choisit ledit polyisocyanate parmi les polyisocyanates aliphatiques, les polyisocyanates cycloaliphatiques, les isocyanurates aliphatiques et leurs mélanges et on le choisit de préférence parmi le 1,4-tétraméthylènediisocyanate, le 1,6-hexaméthylènediisocyanate, le 2,2,4-triméthylhexane-1,6-diisocyanate, le 1,3-bis-[2-(2-(isocyanato)propyl)]benzène (TMXDI), le méta-xylylènediisocyanate, le bis-(fumarate d'isocyanatoéthyle), l'isophoronediiisocyanate (IPDI) et le méthylène-bis-(4-cyclohexylisocyanate).
9. Copolymère greffé selon l'une quelconque des revendications précédentes, dans lequel on choisit lesdits monomères éthyléniquement insaturés dans le groupe constitué des suivants :
 - acide acrylique,
 - acide méthacrylique,
 - esters d'alkyles en C_1 - C_6 d'acide acrylique,
 - esters d'alkyles en C_1 - C_6 d'acide méthacrylique,
 - esters d'hydroxyalkyles en C_1 - C_6 d'acide acrylique,
 - esters d'hydroxyalkyles en C_1 - C_6 d'acide méthacrylique,
 - esters d'alkyles en C_1 - C_6 d'acide fumarique,
 - esters d'hydroxyalkyles en C_1 - C_6 d'acide fumarique,

styrène et
vinyltoluène.

10. Copolymère greffé selon l'une quelconque des revendications précédentes, dans lequel on choisit ledit polyéther parmi les polyétheralcools et les polyétheramines et on le choisit de préférence dans le groupe constitué des polyétheralcools ayant une masse moléculaire moyenne en masse comprise entre 1 200 et 3 000 d (2×10^{-21} g et 5×10^{-21} g).
11. Copolymère greffé selon l'une quelconque des revendications précédentes, dans lequel ledit macromonomère de polyuréthane à terminaison éthylénique a une masse moléculaire moyenne en masse comprise entre environ 3 000 d et 20 000 d (5×10^{-21} g et $33,2 \times 10^{-21}$ g).
12. Copolymère greffé selon la revendication 10, ledit copolymère greffé contenant entre 5 % et 25 % en masse desdits polyétheralcools.
13. Copolymère greffé stabilisé, pouvant être dilué dans l'eau, selon la revendication 1, comprenant le produit réactionnel :
 - A) de 12% en masse à 25 % en masse d'un macromonomère de polyuréthane à terminaison éthylénique qui est le produit réactionnel
 - i) d'un polyisocyanate,
 - ii) d'un composé ayant au moins deux groupements fonctionnels réactifs avec un isocyanate,
 - iii) d'un polyéther ayant un seul groupement fonctionnel réactif avec un isocyanate et
 - iv) d'un monomère monoéthyléniquement insaturé ayant un seul groupement fonctionnel réactif avec un isocyanate;
 - B) d'un ou plusieurs monomères éthyléniquement insaturés, choisis dans le groupe constitué des suivants :
 - esters d'alkyles en C_1-C_6 d'acide acrylique,
 - esters d'alkyles en C_1-C_6 d'acide méthacrylique,
 - esters d'hydroxyalkyles en C_1-C_6 d'acide acrylique,
 - esters d'hydroxyalkyles en C_1-C_6 d'acide méthacrylique,
 - esters d'alkyles en C_1-C_6 d'acide fumarique,
 - esters d'hydroxyalkyles en C_1-C_6 d'acide fumarique,
 - styrène,
 - vinyltoluène,
 - acide acrylique et
 - acide méthacrylique.
14. Pâte de pigment comprenant entre 30 % en masse et 80 % en masse d'un copolymère greffé pouvant être dilué dans l'eau selon l'une quelconque des revendications précédentes, et un ou plusieurs agents de pigmentation.
15. Corps substrat revêtu d'une ou plusieurs couches de base d'une composition de revêtement comprenant un copolymère greffé pouvant être dilué dans l'eau selon l'une quelconque des revendications 1 à 13.